

AD-A140 451

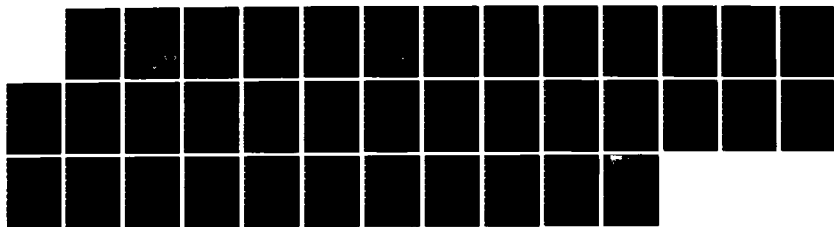
DEVELOPMENT OF METHODS OF EVALUATION EXTENSIONAL
PROPERTIES OF POLYMER SO. (U) RHEOLOGY RESEARCH
GAITHERSBURG MD E A KEARSLEY JUN 83 ARCSL-CR-83076
DAAK11-82-N-0008

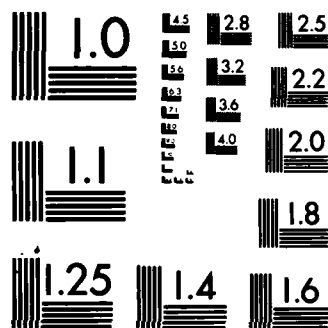
1/1

UNCLASSIFIED

F/G 11/9

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

12

AD



CHEMICAL
SYSTEMS
LABORATORY

US Army Armament Research and Development Command
Aberdeen Proving Ground, Maryland 21010

AD A140451

CONTRACT REPORT ARCSL-CR-83076

DEVELOPMENT OF METHODS OF EVALUATING
EXTENSIONAL PROPERTIES OF POLYMER
SOLUTIONS FROM MEASUREMENTS OF SHEAR

by

E. A. Kearsley

June 1983

RHEOLOGY RESEARCH
9409 Union Place
Gaithersburg, MD 20879

8a

Contract No. DAAK-11-M-0008

DTIC
ELECTE
APR 25 1984
S D B



DTIC FILE COPY

Approved for public release; distribution is unlimited.

84 04 20 002

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

Disposition

Destroy this report when it is no longer needed. Do not return it to the originator.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

DD FORM 1473
1 JAN 73

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

cont'd

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

for the practicality of this procedure for inferring extensional fluid properties.

2
11

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

PREFACE

82

This work was performed under Contract No. DAAK-11-M-0008, Development of Methods of Evaluating Extensional Properties of Polymer Solutions from Measurements of Shear. The work was started in April 1982 and completed in April 1983.

The use of trade names in this report does not constitute an official endorsement or approval of the use of such commercial hardware or software. This report may not be cited for purposes of advertisement.

Reproduction of this document in whole or in part is prohibited except with the permission of the Commander, Chemical Systems Laboratory, ATTN: DRDAR-CLJ-IR, Aberdeen Proving Ground, Maryland 21010. However, the Defense Technical Information Center and the National Technical Information Service are authorized to reproduce the document for US Government purposes.

This report has been approved for release to the public.



Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
PER CALL JC	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Blank

CONTENTS

	Page
1. INTRODUCTION.....	7
2. THEORETICAL BASIS.....	9
3. EXPERIMENTAL	14
3.1 Equipment	14
3.2 Solutions	14
3.3 Procedure	15
4. CALCULATIONS	17
5. CONCLUSIONS AND RECOMMENDATIONS	20
LITERATURE CITED	21
APPENDIXES	
A. Figures.....	23
B. Raw Data.....	29
DISTRIBUTION LIST.....	35

Blank

DEVELOPMENT OF METHODS OF EVALUATING EXTENSIONAL PROPERTIES OF POLYMER SOLUTIONS FROM MEASUREMENTS OF SHEAR

1. INTRODUCTION

Large extensional flow components occur in many important technological processes of liquids. In general, any processing of a liquid using converging or diverging flow will correlate with some extensional properties of the material. On the other hand, most instruments for establishing the rheology of liquids are based upon measurements of simple shearing flows. The few instruments which measure extensional properties of liquids are designed to handle only the thickest of liquids such as polymer melts suitable for spinning into synthetic fibers. There are serious obstacles to adapting these devices to measure polymer solutions. It would be a valuable achievement, therefore, to find a technique of inferring the extensional mechanical properties of polymeric fluids from measurements of shear. We report here a preliminary exploration of the possibility of one such technique to be applied to polymeric solutions of moderate concentration.

There is no purely geometrical relation between the shear properties of a material and the extensional properties. To make a connection, some sort of constitutive conditions must be invoked. For polymeric materials, it is known that realistic constitutive equations are of the hereditary type, that is, the state of stress in the material is taken to depend on the whole history of the deformation of the material. Among the possible hereditary constitutive equations, in recent years the BKZ model^{1,2,3} has proved the most effective in dealing with amorphous polymers and polymer solutions. As will be explained in the next section, the BKZ model has the interesting property that stress relaxation measurements are sufficient to determine the complete mechanical behavior of the material being modelled. Furthermore, isochrones of these stress relaxation measurements have a mathematical character identical with that of a strain energy function of an elastic medium. Indeed, the BKZ model can be used to describe both the entropic elastic mechanism which is the source of rubber elasticity and the mechanisms producing viscous losses in fluids.

This fact underlies the success of the model in dealing with the mechanics of polymeric materials. It is the physics of the entropic mechanism which suggests a connection between shear and extension. Recent work in rubber elasticity has shown that the entropy of deformation is, to a remarkable degree, a superposition of effects from individual principal stretches without cross terms.⁴ Incorporating this idea with the BKZ model allows one to relate the mechanics of extension to the measurements in shear. These matters are discussed in the following section.

The most direct method of applying these theoretical ideas is through stress relaxation measurements in shear. Measurement of stress relaxation of fluids poses certain practical difficulties which limit the range of concentration for which it was possible to obtain good data on solutions. One of the important results of this work is the elucidation of these limitations. The experimental details of the measurement of stress relaxation for five different solutions are given in Section 3. Section 4 discusses the numerical treatment of the measurements. It was found that a very careful and elaborate smoothing of the raw data is necessary in calculating accurate and reliable values of a material function. This process is crucial to the success of this technique. It is illustrated for one sample in Section 4.

Section 5 lists some conclusions and recommendations for continuing work which arose out of this preliminary study.

2. THEORETICAL BASIS

The BKZ model¹ was proposed almost 20 years ago to model non-linear, time-dependent viscoelastic behavior of materials such as elastomers, polymer melts and solutions. Since that time, it has proved to be a practical and accurate model for a wide range of materials and deformation histories. In the case of isothermal flows of homogeneous incompressible fluids, the model may be summarized in the following equation.³

$$\sigma_{ij} = -p\delta_{ij} + 2 \int_{-\infty}^t [U_1(B(t,\tau), t-\tau) B_{ij} - U_2(B(t,\tau), t-\tau) B_{ij}^{-1}] d\tau \quad (1)$$

$$I = \text{tr} B, \quad II = \text{tr} B^{-1}, \quad \det B = 1$$

where σ_{ij} is a component of true stress, p is an arbitrary scalar pressure, I and II are the first and second scalar invariants of B .

τ is a variable of integration which has the significance of time in the past with respect to the present time t , B_{ij} is a component of B , the left relative Cauchy-Green tensor and B_{ij}^{-1} is a component of its inverse. In this equation U is a scalar function of time and of the scalar invariants^{*} I and II respectively. Note that B and thus I and II are calculated from the deformation which maps the configuration at time τ in the past into the configuration at the present time t and therefore they are implicit functions of these times. The function of U is constitutive, that is, it carries a complete description of the mechanical behavior unique to the material it represents and, therefore, it must be measured for each material for which we wish to apply the model. When, for any material, U is completely known as a function of the three dependent variables of the deformation history (I , II and τ) the mechanical behavior of the material is completely specified. U has the character of a time-dependent free-energy.

Stress relaxation experiments play a very fundamental role in BKZ theory. The information carried by the constitutive function U may also be expressed in terms of stress-relaxation functions. Let $\sigma_{SR}(B, \tau)$ represent the stress relaxation function, that is, the residual stress in a specimen at a time τ after being subjected to

* Any scalar function of the tensor B is equal to a function of the scalar invariants of B .

and held at a deformation (represented by tensor B) from a stress-free relaxed state. Then, equation (1) may be re-written in terms of this stress relaxation function as follows

$$\sigma(t) = -pI + \int_{-\infty}^t \sigma_{SR}(B(t,\tau), t-\tau) d\tau \quad (2)$$

This equation says that the stress in a material at a time with any history of deformation is a superposition of stress relaxation functions for deformations representing the change in configuration from times in the past to the present and for relaxation times of the corresponding time interval. In other words, one can completely specify the mechanical behavior of a material by measuring the stress-relaxation function $\sigma_{SR}(B,\tau)$ for all the deformations B and all time intervals τ .

The stress relaxation function, considered as a function of deformation but at a fixed relaxation time is known as an isochrone. An isochrone of a BKZ material has the character of a strain energy function of finite elasticity theory. One can view the characterization of the mechanical properties of a BKZ material as the specification of a time-dependent elastic strain energy function corresponding to a complete set of isochrones of all stress-relaxation functions. Thus, the ideas and theorems of finite elasticity theory can be applied.

In finite elasticity theory, the properties of a material are given by a strain energy function. In the general case, when the strain energy function is not specified further, the behavior of the material in extensional deformations cannot be inferred from its behavior in shear. Recently, Valanis and Landel⁴ have proposed a special form of elastic strain energy function which they showed to model accurately the behavior of elastic materials such as natural rubber and other elastomers. The Valanis-Landel form of elastic strain energy function carries the constitutive information on the elastic behavior of a material in the form of a simple scalar function of one variable. This function can be evaluated either from shear measurements⁵ or from extensional measurements^{5,6}. Consequently, in the case of a Valanis-Landel elastic material

the behavior in extension can be inferred from the behavior in shear. In Valanis-Landel elasticity, the strain energy function of finite elasticity W is given as follows:

$$W = w(\lambda) + w(\mu) + w(\nu) \quad (3)$$

$$\lambda\mu\nu = 1$$

where $w(\lambda)$ is the constitutive function (we shall call the V-L function) and λ, μ, ν are stretches in the three principal directions of the deformation at a point. The second of the equations expresses the fact that the material can be considered incompressible.

To produce simple torsion in a right circular cylinder of an incompressible isotropic elastic material, it has been shown that a torsional moment T must be applied to the ends of the sample⁷:

$$T = 4\pi\psi \int_0^R (W_1 + W_2) r^3 dr \quad (4)$$

and in addition a normal force, N , must be applied parallel to the axis of the cylinder.

$$N = -2\pi\psi^2 \int_0^R (W_1 + 2W_2) r^3 dr \quad (5)$$

Here ψ is the angle of twist per unit length, R is the radius of the cylinder, W_1 and W_2 are partial derivatives of the strain energy density function with respect to the first and second invariants of the deformation tensor. When these equations are put in terms of the V-L function they become

$$T = 2\pi\psi \int_0^R \frac{\lambda^2}{(\lambda^4 - 1)} [\lambda w'(\lambda) - 1/\lambda w'(1/\lambda)] r^3 dr \quad (6)$$

$$N = -\pi\psi^2 \int_0^R \frac{\lambda^2}{(\lambda^2 - 1)(\lambda^4 - 1)} [(\lambda^2 - 2) w'(\lambda) - (2\lambda^2 - 1) 1/\lambda w'(1/\lambda)] r^3 dr \quad (7)$$

where λ is a principal stretch greater than unity given as a function of radius by

$$\lambda(r) = \frac{1}{2}((\psi^2 r^2 + 4)^{\frac{1}{2}} + \psi r) \quad (8)$$

These equations are to be used to evaluate $\lambda w'(\lambda)$ for the elastic material. To proceed, it is necessary to find a method of calculating values at a point from values integrated over the cross section of the cylinder. The procedure of Kearsley and Penn⁸ will accomplish this. Using this procedure and taking derivatives of equations (6) and (7) we obtain

$$\lambda w'(\lambda) - 1/\lambda w'(1/\lambda) = \frac{1}{2\pi\psi R^4} \frac{\lambda^4 - 1}{\lambda^2} (3T + \psi T_\psi) \quad (9)$$

$$(\lambda^2 - 2) \lambda w'(\lambda) - (2\lambda^2 - 1) 1/\lambda w'(1/\lambda) = - \frac{1}{\pi\psi^2 R^4} \frac{(\lambda^2 - 1)(\lambda^4 - 1)}{\lambda^2} (2N_\psi + \psi N_\psi) \quad (10)$$

where T_ψ and N_ψ are the slopes of plots (isochrones) of shear stress and normal stress, respectively, versus the twist. Equations (9) and (10) can be solved for $\lambda w'(\lambda)$ and $1/\lambda w'(1/\lambda)$ for each value of λ , where

$$\lambda = \frac{1}{2}((\psi^2 R^2 + 4)^{\frac{1}{2}} + \psi R) \quad (11)$$

These equations (9), (10) and (11) can be used to evaluate $\lambda w'(\lambda)$ from data on torque and normal force as a function of twist. When $\lambda w'(\lambda)$ is known for all λ , the strain energy function can be constructed.

When the V-L function is measured for all relevant values of λ by this method (or any other method), the elastic response can be calculated for any deformation. For example, if a strand of material of initial cross-section A_0 is stretched to λ times its unstretched length, the force F required is given by

$$F = \frac{\sigma A_0}{\lambda} = \frac{A_0}{\lambda} (\lambda w'(\lambda) - \lambda^{-\frac{1}{2}} w'(\lambda^{-\frac{1}{2}})) \quad (12)$$

Similarly, if a square sheet of initial thickness t and unstretched

side L is stretched biaxially to a larger square of side λL , the forces F acting on each side are give by

$$F = \frac{\sigma L t}{\lambda} = \frac{L t}{\lambda} (\lambda w'(\lambda) - \lambda^{-2} w'(\lambda^{-2})) \quad (13)$$

Thus the extensional properties of an elastic material of the Valanis-Landel type can be measured from experiments on torsion.

In modelling a polymer solution as a BKZ fluid, we take the isochrones of stress relaxation to correspond to an elastic strain energy of the Valanis-Landel type. Then stress relaxation experiments in torsion may be used as shown above to calculate a V-L function for each isochrone. In this way, we find a function $\lambda w'(\lambda, t)$ of two variables (stretch and time) which completely characterizes the non-linear time dependent behavior of the solution. For instance, in extension of a strand of solution, in light of equation (12) for an elastic material, we can write for the viscoelastic polymer solution

$$F(t) = A(t) \int_{-\infty}^t [\lambda w'(\lambda, t-\tau) - \lambda^{-\frac{1}{2}} w'(\lambda^{-\frac{1}{2}}, t-\tau)] d\tau \quad (14)$$

$$\lambda = L(t)/L(\lambda)$$

where $F(t)$ is the force at time t extending the strand, $L(t)$ is the length of the strand at time t and $A(t)$ is the cross sectional area of the strand at time t . To use this equation, the history of the length of the strand is observed from an equilibrium rest position up to time t . This information is then used in equation (14) to calculate force. We could also have written down the obvious generalization of equation (13) to apply to homogeneous biaxial stretching of a sheet of viscoelastic material. In fact, we can write such equations for any deformation history. The important point in this model is that the V-L function measured from experiments on torsion as a function of two variables (stretch and time) contains all the constitutive information necessary to determine the stress for any deformation history of the material.

3. EXPERIMENTAL

3.1 Equipment

Stress relaxation data in torsion was measured with a Rheometrics Mechanical Spectrometer RMS-7200. In general the calibration procedures followed were those given in the operation manual. However, it was found that the angular position of the torsion head was not a linear function of the applied voltage. Consequently, a technique was worked out to calibrate position at small angles ($\pm 10^0$) by observing the deflection on a scale attached to the wall of the laboratory of a spot of light reflected from a mirror fixed on the torsion head. For larger angles, calibration was done directly with a pointer attached to the torsion head reading against a centimeter scale wrapped around a fixed cylinder.

The torsion was achieved between circular plates of 7.22 cm. diameter. The lower plate had a relief well and outer retaining wall to keep extruded material from dripping. As mentioned in the section on procedures, this extruded material was probably the cause of the most serious errors in measurement.

As one check on the operation of the Rheometrics, steady state viscosity of a standard viscosity oil (OB oil, 267 poise at 23.5^0 C) was measured and found to be correct to within better than 5%. Since temperature was not controlled, this accuracy was considered to be adequate for our purposes.

3.2 Solutions

Data was run on solutions of polymethylmethacrylate (PMMA, S-5522) and of Elvacite in diethyl malonate (DEM). The concentrations used were determined by the practical requirements of the Rheometrics measuring device. If the solution was too dilute, the forces generated during deformation were too small to allow accurate data. On the other hand, if solutions were too concentrated, it became impractical to load the solution into the proper cylindrical space for measurement without introducing significant air bubbles into the samples. The usable range of concentrations had to be established by trial and error for each polymer. For PMMA

this range was from about 4% to 6% and for the Elvacite it was from about 19% to 24%. Some initial difficulties in dissolving reproducible samples turned out to be caused by improper cover liners on the wide mouth jars used. The technique finally used consisted of adding powdered polymer to solvent and warming and mixing the resulting suspension by rolling in a sealed glass jar for about a week. The resulting solution showed no sign of inhomogeneity.

Data had to be run within a day of loading the measurement apparatus to keep the evaporation of solvent within acceptable bounds. Of course, all solutions were kept in sealed jars during and after mixing except while measurements were being taken. Table 1. lists the solutions for which relaxation data was taken and the V-L function subsequently calculated.

Table 1. Composition of Solutions

Designation	Solute in 100cc of DEM
P-4	4.163 gm PMMA (S-5522)
P-5	5.117 gm " "
E-20	20.012 gm Elvacite
E-23	23.086 gm "
E-25	25.012 gm "

3.3 Procedure

Solutions to be measured were sucked up with a barrel and plunger device and then extruded onto the lower plate of the torsional apparatus. Great care was taken to minimize the number of air bubbles introduced by this operation and the material was allowed to stand for several minutes after extrusion so that most of the air bubbles could come to the surface and be removed. The upper (conical) plate was then slowly lowered until the solution just began to extrude all around the edge of the platens. Since about 15cc was a typical load of solution and the radius of the platens was 3.61 cm., the spacing when the sample just filled the space between the platens was typically of the order of 3 millimeters. It was impossible to trim the excess sample which

extruded because of its high elasticity. Probably, the chief source of error in the measurements was the effect of this excess material.

All stress relaxation measurements on a given loading were taken within a day to avoid effects caused by evaporation of solvent. Measurements repeated within a day gave no systematic variations. Torque and normal force were recorded simultaneously on a chart recorder during relaxation. Data were then measured by hand from the recording chart for a range of times from $\frac{1}{2}$ sec up to as much as 30 seconds. It was found that at least 15 minutes had to be allowed for relaxation to equilibrium between runs in order to eliminate the effects of earlier runs and to assure reproducible data.

It was necessary to do about six relaxations at each value of shear in order to map out a complete relaxation. This is because different sensitivities of the force and torque scales had to be used to get accurate data on different parts of the relaxation curve. Considerable patience was required.

Table 2, lists the values of maximum shear for which data were taken for each solution

Table 2. Values of maximum shear for relaxation measurements

Solution	Maximum shears						
P-4	3.12	5.72	9.48	11.60	14.24	15.24	19.98
P-5	4.56	5.68	9.08	10.90	13.74	19.72	
E-20	4.44	5.36	7.60	9.14	12.40		
E-23	2.82	3.68	5.42	6.54	7.36	8.68	9.78
E-25	3.70	4.72	6.72	8.66	11.28	11.62	14.26

4. CALCULATIONS

Figure 1 shows one plot of stress relaxation for solution P-5 at a maximum shear of 13.74. The maximum shear, γ_M , is related to the twist ψ by

$$\gamma_M = \psi R \quad (15)$$

The plot is qualitatively representative of the data on any of the samples at fixed shear. To obtain the data of this figure, five individual relaxation experiments were done, each at the same fixed maximum shear but with different settings of sensitivity on the torque and normal force meters to measure overlapping sections of the curve. Error bars have been drawn in at a few points to show how the accuracy of the data deteriorates for relaxation at long times. This problem results from electrical and mechanical noise in the measurement system. An isochrone can be constructed from a set of such relaxation curves over a range of shears. Figure 2 shows isochrones of torque for solution P-4 for times of relaxation ranging from one second to twenty seconds. These isochrones were constructed by taking values of torque for some fixed time of relaxation but at various shears and plotting them versus shear. The curves have been drawn by eye. One can get an idea of the quality of the data from Figure 2. The fact that we can draw smooth curves consistent with the data is very reassuring (and vital to the project, as we shall see) because this cross-plotting is very sensitive to errors.

The quantities T_ψ and N_ψ of equations (9) and (10) are related to the slopes of the isochrones by the equations

$$T_\psi = R \frac{\partial T}{\partial \gamma_M} \quad N_\psi = R \frac{\partial N}{\partial \gamma_M} \quad (16)$$

We first attempted to estimate the slopes by a numerical method rather than by taking them graphically from the plots. Given a sequence of isochronous values of torque, for instance, arranged according to the monotonically increasing shear, the slopes of the end points were taken to be that of a straight line to the neighboring points in the sequence.

For interior points, the slopes were taken as the averages of slopes of such lines weighted by the inverse of the intervals to the next points on the axis. With values of the isochrones and slopes of the isochrones, the V-L function can be calculated from the equation

$$\lambda w'(\lambda, t) = \frac{\lambda^2 - 1}{\lambda} \frac{1}{2\pi\psi^2 R^4} [2(\lambda^2 - 1)(2N + \psi N_\psi) + (\lambda^2 + 2)(\psi^2 T_\psi + 3\psi T)] \quad (17)$$

which can be derived from equations (9) and (10). In this equation T and N are considered as functions of relaxation time and of twist. For each twist two values of λ can be calculated, viz.:

$$\lambda = \frac{1}{2}((\psi^2 R^2 + 4)^{\frac{1}{2}} \pm \psi R) \quad (18)$$

Calculations of the V-L function with data treated only as described above generated scattered points which did not determine a smooth curve. The difficulty was eventually traced to insufficient smoothing of the data. The term in N and its derivative in equation (17) is of opposite sign but approximately the same magnitude as the term in T and its derivative. Consequently, the calculation of the V-L function involves the small difference between large quantities. What is more, these large quantities themselves contain the calculated slopes of experimental data. For this reason, very careful and sophisticated calculation methods are required.

Ultimately, the following procedure was adapted. The raw data points were plotted on logarithm plots and a smooth curve consistent with the data was drawn by eye. The slopes of these curves at the values of γ of the data points were calculated graphically. The values of slope for fixed γ were then plotted versus relaxation times. By an iterative process, the original data was smoothed until the calculated slopes for fixed γ also fell on a smooth curve systematically changing with t . This process was necessarily a very tedious one. Figure 3 shows the results for solution E-23 as a plot of the derivative of the V-L function for four times of relaxation spaced logarithmically. In Figure 4 we show

a part of one of the curves of Figure 3 plotted with the corresponding results from the first numerical calculation of slopes. It is very clear from these two figures that the complex and tedious procedure of treating the raw data is necessary and sufficient to produce a reasonable plot of the derivative of the V-L function.

Since the slope of the V-L function is negative for values of λ less than one, Figure 3 is a plot of the absolute value of the derivative of the V-L function. By definition, this quantity is zero at λ of one so that there is a corresponding point at minus infinity which cannot be shown. The smallest values for λ less than one at large relaxation times may still be showing "noise" in the plots of Figure 3. From a practical point of view, this is not serious since in calculations of stress the function plotted in the figure always appears in combinations involving two values of λ . For extensions, for instance, there will be a λ greater than one as well as a λ less than one. In that case the "noise" of the λ less than one will not seriously affect the combination.

Table 3. gives a set of smoothed data used in calculating one of the curves of Figure 3.

Table 3. Sample Smoothed Data for Solution E-23
at time two seconds

γ	T	N	slope log T	slope log N	W_1	W_2
2.82	67	31.5	.663	1.35	.134	.0145
3.68	77	44.6	.388	1.26	.111	.0097
5.42	82	70	.002	1.10	.064	.0133
6.54	81	85	-.131	.959	.049	.0113
7.36	79	95	-.249	.903	.039	.0115
8.68	76	109	-.335	.795	.030	.0098
9.78	73	118	-.410	.740	.024	.0085

5. CONCLUSIONS AND RECOMMENDATIONS

A model of the mechanical behavior of polymer solutions has been formulated which can be used to infer extensional properties from measurements of shear. The model is consistent with our experience of measurements and phenomena in shear.

Measurements of five solutions show promise for the practicality of this technique but suggest that further experience is necessary.

There are practical experimental limitations in measuring stress relaxation which limit the range of concentrations of a polymer solution which can be measured. Therefore, methods of extrapolation in concentration need to be worked out.

Very careful and complex treatment of the data is needed in order to get good results. More efficient methods of accomplishing this treatment should be worked out. If possible, a computer program should be developed to accomplish this task.

The technique should be tested for its applicability to extensional flows. For this purpose, theoretical and experimental studies of some convenient extensional flow should eventually be initiated.

Ultimately, through measurements by the method proposed here, various features of the V-L function selected from theoretical and experimental considerations should be examined for their effect on the stability of extensional flows. In this way, quantitative measurements can be correlated with data on breakup of jets.

LITERATURE CITED

1. Bernstein, B., E.A. Kearsley and L.J. Zapas. Thermodynamics of Perfect Elastic Fluids, Jour. Research National Bur. Standards 68B, pp 103-113 (1964).
2. Bernstein, E., E.A. Kearsley and L.J. Zapas. A Study of Stress Relaxation with Finite Strain, Transact. Soc. Rheology 7, pp 391-410 (1963).
3. Bernstein, B. Time Dependent Behavior of an Incompressible Elastic Fluid, Acta Mechanica, II/4, p. 329 (1966).
4. Valanis, K.C. and R.F. Landel. The Strain-Energy Functions of a Hyperelastic Material in Terms of Extension Ratios, J. Appl. Phys., 38, p 2997 (1967).
5. Kearsley, E.A. and L.J. Zapas. Some Methods of Measurement of an Elastic Strain Energy Function of the Valanis-Landel Type, Jour. Rheology 24, pp 483-500 (1980).
6. Kearsley, E.A. Determining an Elastic Strain-Energy Function from Torsion and Simple Extension, Jour. Appl. Phys. 51 (8), 4541-2, (1980).
7. Rivlin R.S. Large Elastic Deformations, in Rheology, pp. 352-385, Vol. I, editor F.R. Eirich, Academic Press, New York 1956.
8. Penn, R.W. and E.A. Kearsley. The Scaling Law for Finite Torsion of Elastic Cylinders, Transact. Soc. Rheology 20, pp 227-238 (1976).

Blank

APPENDIX A

FIGURES

STRESS RELAXATION OF TORQUE OF SOLUTION P-5

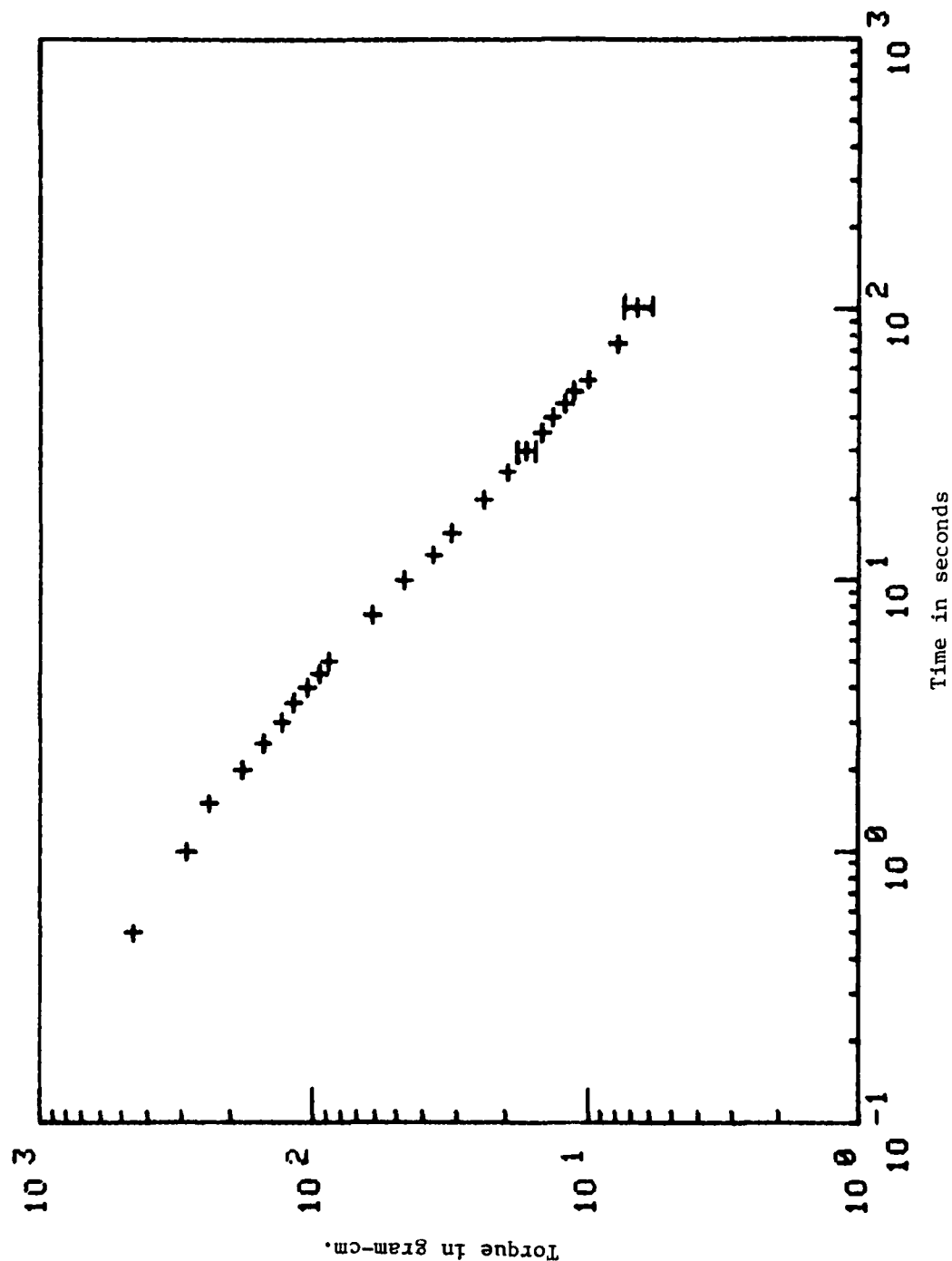


Figure 1

A plot of stress relaxation of torque in solution P-5 at a shear of 13.74. Torque is in units of gram-cm. and time in seconds. This curve is a composite of data from five relaxation experiments. Similar data were taken for a variety of shears and also for the relaxation of normal force.

TORQUE ISOCHRONES OF SOLUTION P-5

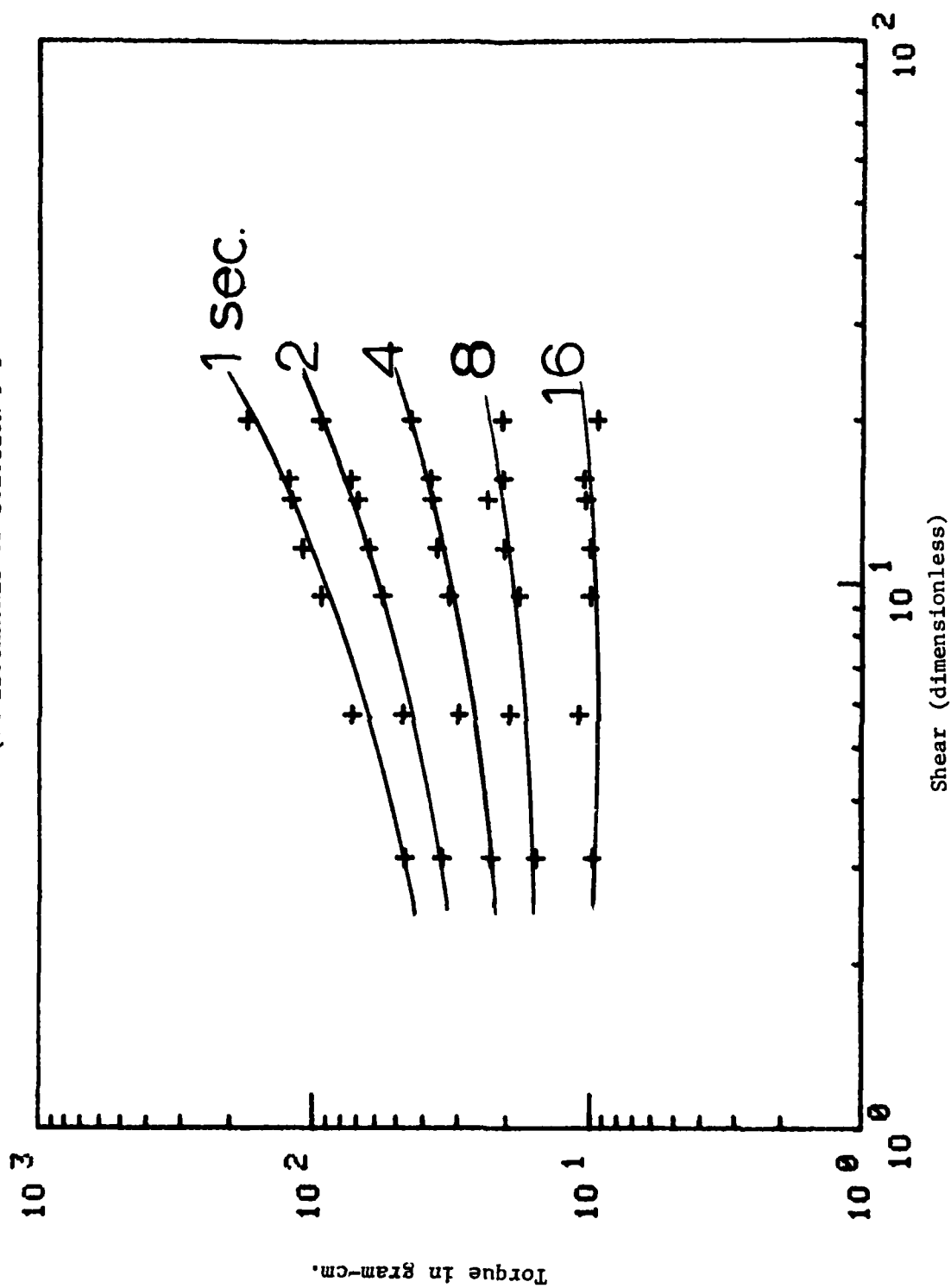


Figure 2

Isochrones formed from stress relaxation data of solution P-4 for a set of seven values of shear. Similar isochrones were formed from data of normal force relaxation.

SMOOTHED CALCULATIONS OF SOLUTION E-23

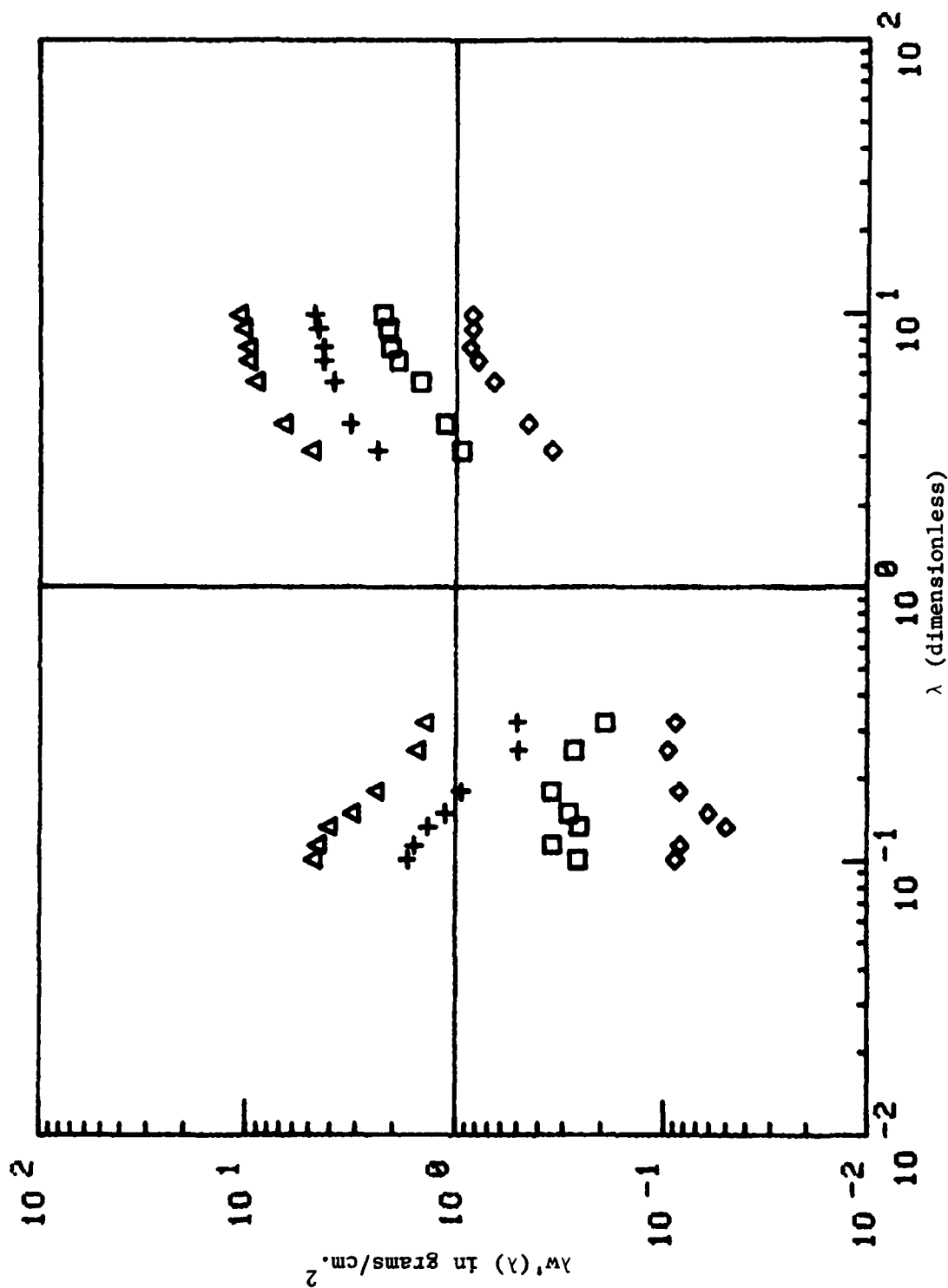


Figure 3

Calculated values of the function $w'(\lambda)$ for solution E-23. From this data it is possible to calculate the response of the material to general deformation histories.

A COMPARISON OF SMOOTHED AND UNSMOOTHED RESULTS

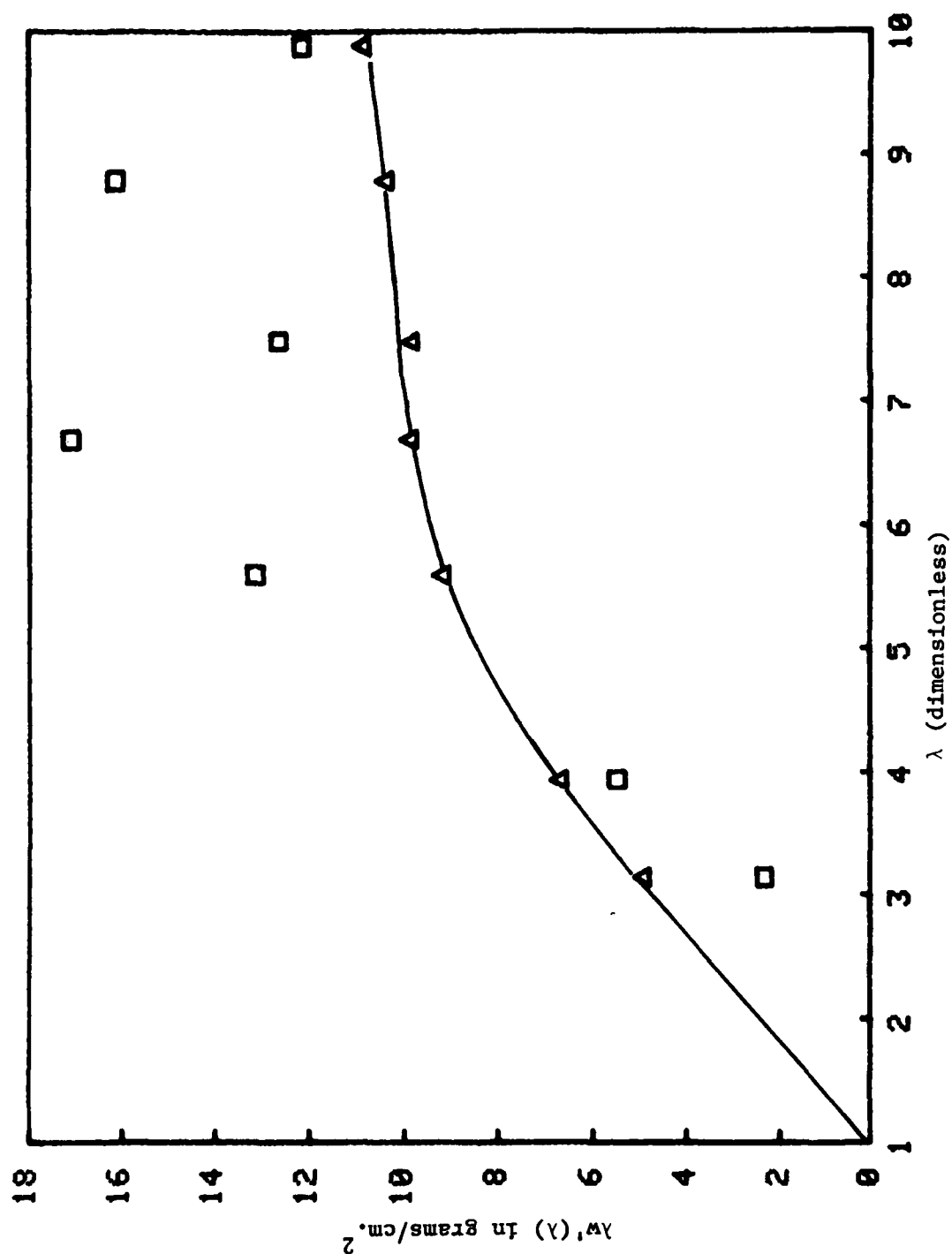


Figure 4

A comparison of the calculation of $\lambda w'(\lambda)$ from raw data and smoothed data. Smoothing was done in the time variable as well as the shear. It is evident that smoothing is necessary to produce usable results.

Blank

APPENDIX B

RAW DATA

Raw Data for Solution P-4

shear	3.12	5.72	9.48	11.6	14.24	15.54	19.98
time units	TORQUE						
1	63.5	108		185	189	214	345
2	47.0	73	94	110	121	124	175
3	39.0	57	70	84	90	95	120
4	34.5	48	56.5	63.5	70	73.5	95
5	29.2	41.5	47.5	55	59	60	77
6	26.2	37	41.5	47	49	50.5	63
7	23.8	32.8	36.5	41	42.5	43.5	52
8	22.8	30	32.5	36	37.5	38	45
9	21.4	27.8	29.5	33	32.5	34	39
10	20.0	25.8	29	28	30	30.5	35
15	15.7	19.6	18	20.5	23.6	20.6	21
20	12.9	15.2	14.2	15.5	16.2	15.6	15.5
25	11.0	12.8	11.9	12.0	13.4	12.4	11.9
30	9.8	11.0	10	10	10.4	10.5	9.5
40	8.0	8.4	8	9	7.4	7.7	
50	6.8	6.6	6.2		6.0	6.2	

NORMAL FORCE

1		97.5		301			
2	22.5	58.5	132	173	275	285	575
3	18.0	49	97	127	198	205	360
4	15.2	41	76.5	104	151	155	265
5	13.3	34.7	60.4	91	120	127.5	226
6	12.2	30.3	55	73	101	107.5	182
7	10.9	27.3	48.5	68.5	86	96.5	152
8	10.1	25	43.5	61	76	84.5	132
9	9.5	23	39.5	55	68	75	113
10	8.55	21.3	35.5	50.5	61	67.5	99
15	6.3	16.4	24.5	35	41	45	60.5
20	5.75	13.2	18.6	27	30	35.5	43.5
25	4.85	11.2	15.0	22	25	26.5	33
30	4.10	9.7	12.5	18.5	22.3	21.9	27
40	3.25	7.6	8.4	14.5	16.7	16.1	19.5
50	2.70	6.4	7.5		13.2	12.7	15

Torque in gram-centimeters, normal force in grams, time units at 0.472 seconds.

Raw Data for Solution P-5

shear	4.56	5.68	9.08	10.90	13.74	19.72
time units	TORQUE					
1	186	200	300	350	450	620
2	131	143	192	235	286	410
3	107	116	155	180	238	300
4	92	100	128	151	180	230
5	82	89	113	130	152	190
6	72.5	80	104	114	130	160
7	68	71	93	101	117	142
8	63	65	84	91.5	105	127
9	58.5	61	77	83	95	112
10	55.5	58	71.5	77	87.5	100
15	42.4	45	54	56	61	67
20	35.8	37.5	43.5	46	47	47.5
25	31.6	32.5	36.5	39	36.5	35.8
30	27.8	29	32	34.5	31.6	29.2
40	23.2	24.5	25.5	27.4	23.8	22.1
50	20.1	20.6	21	22.8	19.7	17.7
60	18.0	18.2	18.5	19.8	16.7	14.7
70	16.2	16.2	16.5	17.4	14.7	12.7
80		14.9		16	13.5	11.3
90				14.4	12.2	10.3
100				13.2	11.2	9.3
110				12.6	10.0	8.7
150					7.8	
200					6.6	

NORMAL FORCE						
1	112	158				
2	79	115	232	320	553	1110
3	65	97	190	260	413	780
4	56	84	163	222	530	610
5	50	75	143	186	283	507
6	46	67	128	162	243	427
7	42	62	114	145	216	372.5
8	39	57	105	130	194	330
9	37	53.8	97.5	120	177	295
10	35	50.5	90.5	111	163	267.5
15	27.5	39	68.5	82	116	172
20	23	32.8	56	65	90	128
25	20	28	47	56	73	103
30	17.5	25	41	49	61	84
40	14.3	19.6	33	38.5	46	62.5
50	12.3	16.6	28.3	32	37	49.5
60	10.6	14.4	23.8	27.5	31	41
70	9.5	12.8	21	25.5	27	35.5
80		11.4		22.8	23	28
90				20.5	21.5	24
100				18.8	19.7	21.5
110				17.2	17.9	19.5
150					13.3	
200					10.3	

Torque in gram-centimeters, normal force in grams, time units at 0.472 seconds.

Raw Data for Solution E-20

shear	2.22	2.68	3.80	4.57	6.20
time units	TORQUE				
2	69	70	60	64	64
3	41	38	37.5	38	36
4	27	24	24.5	25	22
5	20	18	17.5	18	14.6
6	15.8	13	13.5	13.5	10.2
7	12.0	10	10.3	10.5	8.2
8	9.8	7.9	8.6	7.8	7.0
9	7.8	6.3	6.9	6.3	5.7
10	6.8	5.2	5.6	5.2	4.8
15	4.0	2.4	2.5	7.3	1.9
20	2.8	1.6	1.5		1.1
25		1.2			

NORMAL FORCE

2	42	59	85	115	144
3	32	34	48	57	70
4	23.2	22	29	34	43
5	15.6	15.5	20	24	31
6	11.7	10.8	15.5	17.5	22.5
7	8.6	8.8	12.0	13.4	18.5
8	6.8	6.8	9	10.4	13.5
9	5.3	5.4	8.2	8.0	10.5
10	4.0	4.4	5.8	6.4	8.5
15	1.8	1.8	2.4	2.6	3.5
20	0.8	0.8			
25		0.4			

Torque in gram-centimeters, normal force in grams, time units at 0.472 seconds.

Raw Data for Solution E-23

shear	2.82	3.68	5.42	6.54	7.36	8.68	9.78
time units	TORQUE						
1			386			380	352
2	140	144	189	216	183	180	174
3	91	109	117	122	115	110	104
4	67	77	82	86	79	75	73
5	52	56	63	66	59	57	56
6	43	45	49	50	47	45	43
7	34.5	37	40	39	38	37	35
8	29	30	32	32.5	31.5	30	29
9	24.5	25.5	27	27.4	26.4	25	24
10	21.5	22.1	23.3	23.2	22.6	21.5	20
15	12	12	13.8	12.5	12.3	11.5	11
20	6.8	7.6	8.7	7.5	7.5	7.2	6.9
25	4.8	5.0	5.7	5.3	4.9	4.9	5.1
30	3.5	3.6	4.1	3.9	3.5	3.5	3.8
35	2.7	2.4	2.5	3.0	2.5	2.5	3.1
40				2.4			2.4
NORMAL FORCE							
1	140	203	390	505		750	940
2	69	107	166	206	235	280	300
3	44.5	61.5	105	116	137	163	175
4	31.5	44.8	70	82	94	109	117
5	24	33.8	53.5	62.5	68	80	87
6	19	26.3	41	53.5	54.5	62	67
7	15.4	21.8	33	39	43	50	53
8	12.8	18	27.5	32.8	36.5	41	43.5
9	10.8	15.1	23.5	27.8	30.3	33	36.8
10	9.5	12.8	20.3	23.7	26	29	31.3
15	5	6.8	10.6	12.5	13.4	15.2	16.2
20	3.2	4	6.7	7.6	8.3	9.2	10
25	2.2	3.8	4.4	4.9	5.4	6.2	6.6
30	1.5	1.9	3.1	3.6	3.7	4.4	4.8
35	1.1	1.5	2.3	2.6	2.6	3.2	3.4
40				1.9		2.7	2.6

Torque in gram-centimeters, normal force in grams, time units at 0.472 seconds.

Raw Data for Solution E-24

shear	1.85	2.36	3.36	4.33	5.64	5.81	7.13
time units	TORQUE						
2	318	348	368	390	385	374	356
3	218	232	254	276	255	240	232
4	163	184	191	194	187	182	162
5	130	142	153	150	146	135	123
6	108	115	124	120	115	107	98
7	92	97	103	100	93	89	80
8	78	82	90	84	80	73.5	67
9	67	72	75	73	70	65	58
10	59	62	66	64	60.5	56	50
15	35.4	37	38	36	35.0	33	29
20	24.2	24.8	25.5	25	22.3	22	21
25	17.8	17.2	19	18	16.8	16	14.8
30		13.0	14.5	14	13.0	12.3	11.0
35		10	11.5	11.4	10.8	9.8	9.0
40				10.8	9.0	8.0	

NORMAL FORCE							
2	210	280	533	610	700	875	1060
3	135	194	328	398	452	520	590
4	101	142	230	288	317	358	398
5	80	110	178	215	237	265	290
6	64.5	89	140	174	190	207	227
7	54.3	73.5	119	143	155	169	189
8	45.9	62	108	120	130	141	158
9	39.3	53.5	86	102	111	121	136
10	34.3	47	74	98	97.5	107	118
15	19.4	26.5	42	49	54.8	60.5	65
20	12.5	17	27	32	34.8	38.5	42
25	8.5	11.8	18.5	22.5	24.3	27	29
30		8.3	13	16.3	17.3	20	21.5
35			10	12.3	13.3	15	16.5
40				9.5	10.0	11	

Torque in gram-centimeters, normal force in grams, time units at 0.472 seconds.

END

FILMED

5-84

DTIC